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(56) Documents Cited
EP 0678560 A2 JP 090151333 A2
Chemical Abstracts, abstr no 129:303645 & JP 100251535 A2 22 .09.1998

(58) Field of Search
Online: CAS ONLINE

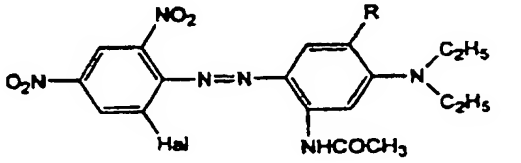
(54) Abstract Title

Dye composition for dyeing fibres based on mixture of at least three N-ethyl-N-substituted 4-(2-halo-4-nitro-6-[halo/nitro]phenyl)azoaniline derivatives

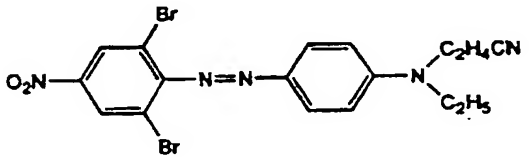
(57) Dye compositions for dyeing fibres, particularly polyester fibres and their blends, comprise (a) from 20 to 40% of at least one azo dye of structure (I); (b) from 20 to 40% of at least one azo dye of structure (II); and (c) from 10 to 50% of a dye of structure (III), the percentages being by weight of total dye in the composition.

Preferably, Hal is bromine in both (I) and (II), and the composition contains an overall dye content of 40% and 60% by weight of lignin sulphonate dispersant. Such compositions provide strong, economical black shades of pleasing tone, especially when combined with an orange or red azo dye, such as one of formula (IV).

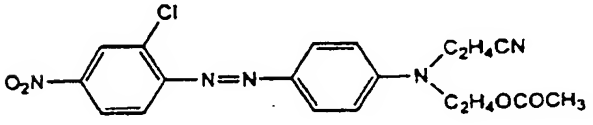
Methods of mixing such dye compositions (by mixing the component dyes and by co-coupling the precursors of compounds of formulae (I) and (II)), and methods of dyeing fibres with the dye compositions, are also described.



(I), R = H, Hal = Cl or Br
(II), R = OMe, Hal = Cl or Br



(III)



(IV)

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The claims were filed later than the filing date but within the period prescribed by Rule 25(1) of the Patents Rules 1995.

DESCRIPTION

DYE COMPOSITION AND METHOD OF DYEING FIBRES

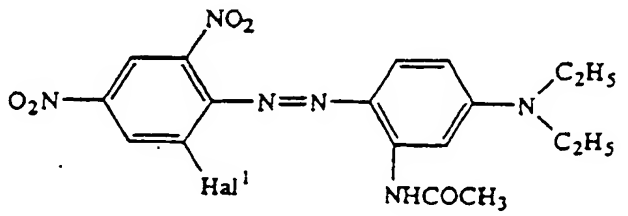
The present invention relates to dye compositions for dyeing fibres, such as synthetic fibres, particularly polyester fibres and their blends, a method of making the dye compositions and a method of dyeing fibres using the dye compositions.

Mixtures of azo disperse dyes are well-known for the dyeing of synthetic fibres particularly polyester fibres and their blends. A number of these mixtures provide black shades.

GB 1 582 743 and FR 2 388 861 disclose dye mixtures which contain dyes of formulae (I) and (II) as illustrated hereafter, and the use of such mixtures as colourants for polyester textile material and for polyester/cotton blends. The use of such mixtures which contain dyes of only type (I) and (II) gives blue dyeings upon either of the textile materials employed.

According to a first aspect of the present invention there is provided a dye composition for dyeing fibres comprising:

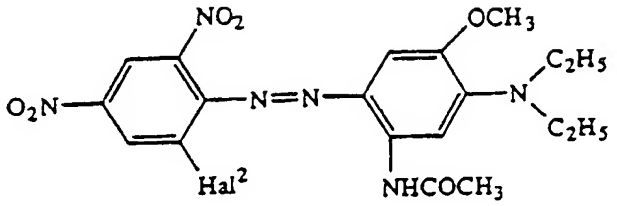
(a) from 20 to 40% by weight of total dye in the composition of at least one azo dye of structure I:



(I)

where Hal^1 is chlorine or bromine;

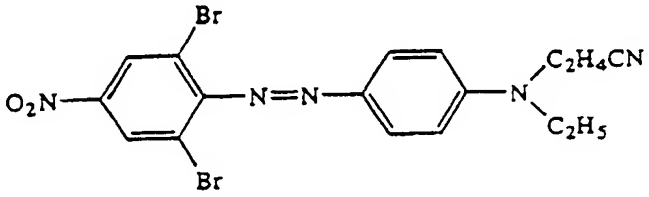
(b) from 20 to 40% by weight of total dye in the composition of at least one azo dye of structure II:



(II)

wherein Hal^2 is chlorine or bromine; and

(c) from 10 to 50% by weight of total dye in the composition of a dye of structure III:



(III)

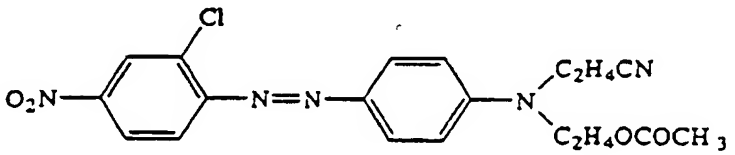
Preferably Hal^1 and Hal^2 are bromine. Dye III is an orange dye.

The current invention provides dye compositions which may be employed to impart a black colouration to synthetic fibres and to their blends with natural fibres. The black colouration imparted to the textile may be of a greenish, a reddish or a bluish tone depending upon the ratios of the three dyes employed, and this variation in the exact tone may be further adjusted by the addition of a fourth dye to the dye composition.

The advantage of the compositions of this invention over compositions employed in the prior art, is the ability to provide strong, economical black shades of pleasing tone from component dyes which are not known skin sensitisers. The compositions are robust in application properties, giving synergistic build up on polyester, and may be described as strong blacks in that the formulated compositions with adjuvants, when applied at 2.5-2.7% on weight of fibre, produce a B/DK depth of shade. This depth of shade is defined by the British Standards Institute, BS2661:SDM:1961, clause 10, and by the Society of Dyers and Colourists Standard Methods, 3rd Edition, page 7, clause 10.

The fourth dye may be advantageously chosen from, for example, a wide range of orange or red azo disperse dyes.

In a preferred embodiment of the invention, the fourth dye has the structure (IV):



(IV)

This dye IV is a red azo disperse dye. Preferably, dye IV forms from 0 to 30% by weight of total dye in the composition. Depending on the proportions of the four dyes, dye IV can impart a pleasing blue-black tone to the dye composition.

The dye composition preferably contains from 20 to 60% of dyes by weight of the total weight of the composition, and/or additionally contains from 40 to 80% of a dispersant or of a plurality of dispersants. Lignin sulphonate can be used as a dispersant.

The novel dye compositions may also contain other non-dye components which, typically, enhance the dyeing properties of dye compositions in the dyeing process. These components include, for example, lignin sulphonates and the products of sulphonation or sulphomethylation of the condensates of formaldehyde with aromatic compounds.

The dye compositions may be prepared in a conventional manner, for instance by mixing the dye components in the stated weight ratios.

According to a second aspect of the present invention, therefore, there is provided a method of making a dye composition according to the present invention, comprising mixing the dyes in the stated weight ratios.

They may also, in the case of dyes of formula (I) and (II), be prepared by the technique known as co-coupling. This technique, known to those skilled in the art, involves the simultaneous coupling of the common diazonium salt from a 2-halo-4,6-dinitroaniline with the mixed coupling tertiary amines that yield dyes (I) and (II).

A third aspect of the present invention therefore provides a method of making a dye composition according to the present invention, comprising co-coupling these or other compounds.

The dye mixtures may also be prepared by the admixture of ready-

prepared dye formulations of the respective individual dyestuffs.

According to a fourth aspect of the present invention, there is provided a method of dyeing fibres comprising contacting fibres with a dye composition of the present invention in a dye bath. The dye bath is usually a dispersion of the dye composition in water.

Preferably, the dye bath is at a raised temperature. Preferably after the fibres have been introduced into the dye bath, the dye bath is gradually heated to 100-150°C, more preferably to 130°C.

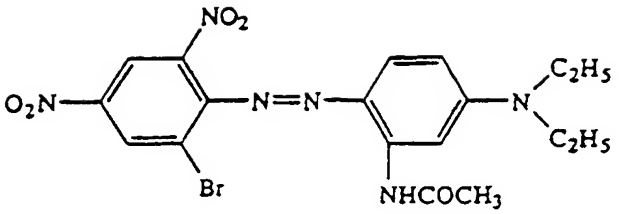
Preferably, the fibres are left in the hot dye bath for one hour after the maximum temperature has been achieved. The dye bath is then preferably gradually cooled (usually to 40-70°C) before removing the fibres, and preferably the fibres are then rinsed. The fibres are preferably synthetic fibres, more preferably polyester fibres or blends thereof. The method is suitable for dyeing fibres in the form of textile fabrics.

The method of dyeing preferably also comprises later steps of reduction clearing the fibre, rinsing the fibre, drying the fibre, and/or stentering the fibre.

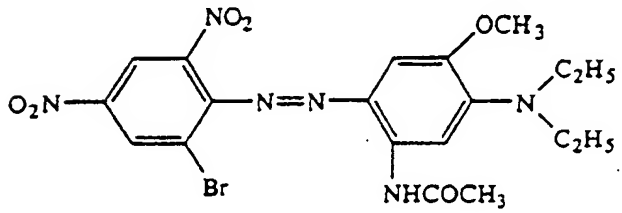
Examples

A specific embodiment of the present invention will now be described, by way of example only. The following examples use the following four specific dyes:-

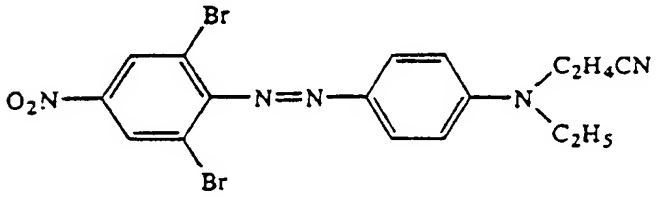
Dye 1



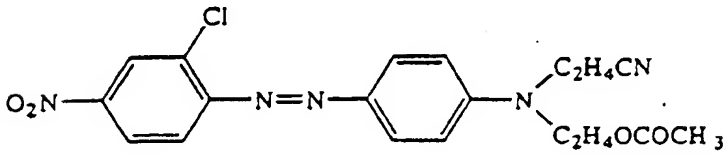
Dye 2



Dye 3



Dye 4



These four dyes are mixed together in the proportions shown in Table 1 to obtain the shades shown (after 2.5% dyeing).

The dyeing method is as follows:

A 4g piece of polyester textile is introduced into 60ml of dyeing liquor containing 2.5% by weight of the dyestuff composition based on the weight of

polyester. The dye compositions contain in each case an overall dye content of 40% and 60% by weight of lignin sulphonate dispersant. The dyeing liquor is prepared by the dissolution of 1ml/1 of a condensation product of naphthalene sulphonic acid with formaldehyde followed by adjustment of the pH to 4.5 using acetic acid. The dyeing liquor is heated to 130°C at the rate of 2°C/min in an infra-red dyeing machine until the temperature reaches 130°C, and this temperature is maintained for one hour. The dyeing tube is then cooled at 2°C/min to 50°C before the textile is removed from the liquor and rinsed with copious cold water.

The dyed polyester textile is then reduction cleared at 70°C for 20 min with a solution containing 2g/1 sodium dithionite, 2g/1 caustic soda and 1g/1 of an addition product of a fatty acid ester with 20 mol of ethylene oxide. Finally the textile is rinsed, dried and stentered at 180°C for 30 seconds.

Alternatively, the dye compositions may be applied to synthetic textiles using other methods known to those skilled in the art.

The dyeing results for six different compositions are now shown in Table 1. Although all six examples shown resulted in aesthetically pleasing shades, Example No. 6 represents a particularly aesthetically pleasing and commercially important bluish-black colouration.

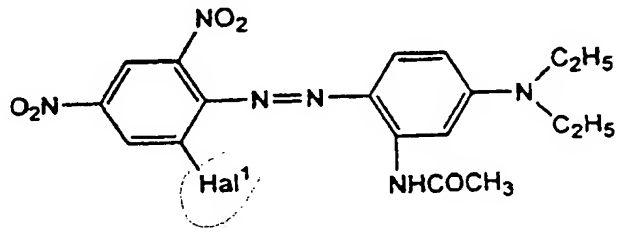
Table 1

Example No.	% by weight of total dye in the dye composition				Shade obtained by 2.5% dyeing
	DYE 1	DYE 2	DYE 3	DYE 4	
1	22	28	30	20	Greenish Black
2	32	28	30	10	Bluish Black
3	31	31	20	18	Reddish Black
4	32	33	35	-	Greenish Black
5	20	20	45	15	Orange Black
6	28	27	30	15	Bluish Black

CLAIMS

1. A dye composition for dyeing fibres comprising:

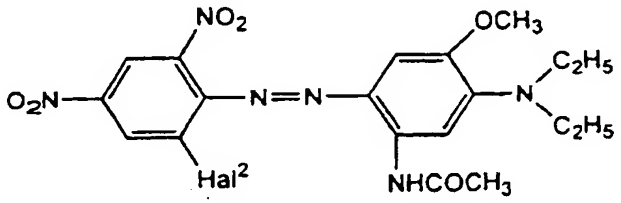
(a) from 20 to 40% by weight of total dye in the composition of at least one azo dye of structure I:



(I)

where Hal^1 is chlorine or bromine;

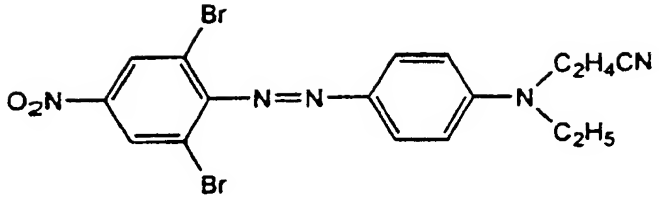
(b) from 20 to 40% by weight of total dye in the composition of at least one azo dye of structure II:



(II)

wherein Hal^2 is chlorine or bromine; and

(c) from 10 to 50% by weight of total dye in the composition of a dye of structure III:



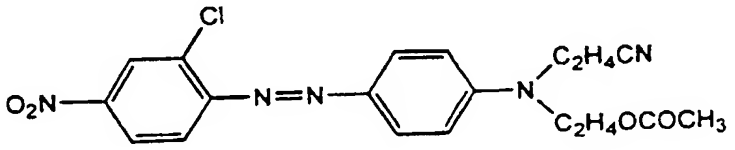
(III)

2. A dye composition as claimed in claim 1, wherein Hal^1 and Hal^2 are bromine.

3. A dye composition as claimed in claim 1 or 2 additionally comprising a fourth dye.

4. A dye composition as claimed in claim 3, wherein the fourth dye comprises an orange or red azo disperse dye.

5. A dye composition as claimed in claim 3, wherein the fourth dye has the structure (IV):



(IV)

6. A dye composition as claimed in claim 5, wherein dye IV forms from 0 to 30% by weight of total dye in the composition.

7. A dye composition as claimed in any one of the preceding claims, wherein the dye composition contains from 20 to 60% of dyes by weight of the total weight of the composition, and/or additionally contains from 40 to 80% of a dispersant or of a plurality of dispersants.

8. A method of making a dye composition as claimed in any one of the preceding claims, comprising mixing the dyes in the stated weight ratios.

9. A method of making a dye composition as claimed in any one of claims 1 to 7, comprising co-coupling compounds to prepare the dyes of formula (I) and/or (II).

10. A method as claimed in claim 9, wherein the method involves the simultaneous coupling of the common diazonium salt from a 2-halo-4,6-dinitroaniline with the mixed coupling tertiary amines that yield dyes (I) and (II).

11. A method of dyeing fibres comprising contacting fibres with a dye composition as claimed in any one of claims 1 to 7 in a dye bath.

12. A method as claimed in claim 11, wherein the dye bath is a dispersion of the dye composition in water.

13. A method as claimed in claim 11 or 12, wherein the dye bath is at a raised temperature.

14. A method as claimed in claim 11 or 12, wherein after the fibres have been introduced into the dye bath, the dye bath is gradually heated to 100-150°C.

15. A method as claimed in claim 14, wherein after the fibres have been introduced into the dye bath, the dye bath is gradually heated to 130°C.

16. A method as claimed in any one of claims 11 to 15, comprising the subsequent steps of cooling the dye bath before removing the fibres, and then rinsing the fibres.

17. A method as claimed in claim 16, wherein the dye bath is gradually cooled to 40-70°C before removing the fibres.

18. Fibres or a textile fabric dyed by the method as defined in any one of claims 11 to 17.

19. A dye composition, a method, fibres or a textile fabric as claimed in any one of the preceding claims, wherein the fibres are polyester fibres or blends thereof.

20. A dye composition, a method, fibres or a textile fabric substantially as herein described in any of the examples.

The Patent Office

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Application No: GB 9809318.0 **Examiner:** Stephen Quick
Claims searched: 1-20 **Date of search:** 23 July 1999

Patents Act 1977
Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.Q):

Int Cl (Ed.6):

Other: Online: CAS ONLINE

Documents considered to be relevant:

Category	Identity of document and relevant passage		Relevant to claims
X	EP 0678560 A2	(NIPPON KAYAKU KABUSHIKI KAISHA), see whole document, especially examples 1-16, noting compound (3) on page 7 corresponds to present compound I, compound (4) on page 7 corresponds to present compound II and CI Disperse Orange 37 is the dichloro equivalent of present compound III	1-20
X	JP 090151333 A2	(DAISTAR JAPAN) 10.06.1997, see page (6) (table, composition nos 4 & 5; and formulae [I], [II] & [III-1], noting that latter is the dichloro equivalent of present compound III); see also Chemical Abstracts, abstr no 127:96565, WPI Abstract Accession No 97-359235/33 & PAJ abstract; dye mixture for the dyeing of polyester fibres	1-20
A	Chemical Abstracts, abstr no 129:303645 & JP 100251535 A2 22.09.1998, see abstract and compounds RN 52697-38-8, 55281-26-0 & 56548-64-2		-

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.